REPORT DOCUMENTATION PAGE

1. REPORT DATE (DD-MM-YYYY) 07-05-2008	2. REPORT TYPE Technical Paper	3. DATES COVERED (From - To)

4. TITLE AND SUBTITLE

Design of Energetic Ionic Liquids (Preprint)

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

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5d. PROJECT NUMBER
23030423

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/RZSP
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8. PERFORMING ORGANIZATION REPORT NUMBER

AFRL-RZ-ED-TP-2008-183

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

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10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S NUMBER(S)
AFRL-RZ-ED-TP-2008-183

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited (PA #08207A).

14. ABSTRACT

An essential need of the US Air Force is the discovery, development, and fielding of new, energetic materials for advanced chemical propulsion in space and missile applications. Some of the key factors driving the requirement for new chemical propellants include: (a) improved performance in terms of increased specific impulse and density, (b) reduced sensitivity to external stimuli such as impact, friction, shock, and electrostatic discharge, and (c) mitigation of environmental and toxicological hazards (and the resulting costs) associated with currently used propellants.

The overall objective of the Design of Energetic Ionic Liquids challenge project is to address several key technical issues and challenges associated with the characterization, design, and development of ILs as new monopropellants. Among these, for example, are a fundamental understanding of the (in)stability of ILs, the intrinsic nature of the short- and long-range structure and interactions between the component ions, and identification of the key steps in the initial stages of decomposition and combustion. A hierarchy of computational approaches is employed, including atomistic, high-level quantum chemical methods applied to individual ions and ion clusters, condensed phase atomistic molecular dynamics simulations utilizing polarizable force fields, and mesoscale-level simulations of bulk ionic liquids based upon multiscale coarse graining techniques.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Dr. Jerry A. Boatz
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified	SAR	6	19b. TELEPHONE NUMBER (include area code) N/A

Design of Energetic Ionic Liquids (PREPRINT)

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Abstract

An essential need of the US Air Force is the discovery, development, and fielding of new, energetic materials for advanced chemical propulsion in space and missile applications. Some of the key factors driving the requirement for new chemical propellants include: (a) improved performance in terms of increased specific impulse and density, (b) reduced sensitivity to external stimuli such as impact, friction, shock, and electrostatic discharge, and (c) mitigation of environmental and toxicological hazards (and the resulting costs) associated with currently used propellants.

A class of compounds which can potentially meet these requirements is known as ionic Liquids (ILs), which are chemical salts with unusually low melting points. The physical and chemical properties of ILs render them useful for many purposes, most notably as environmentally benign ("green") solvents/reaction media but also as catalysts, electrolytes, etc. From a Department of Defense (DoD) perspective, ILs are being explored as new propellants, explosives, and munitions. The Air Force, in particular, is interested in ILs as potential replacements for currently used monopropellants such as hydrazine – which is carcinogenic, highly toxic, and has relatively modest performance characteristics. In contrast, many ILs have superior densities and specific impulses as well as significantly reduced sensitivity and toxicity characteristics. Furthermore, their properties can be carefully tuned via the choice of the component ions.

The overall objective of the Design of Energetic Ionic Liquids challenge project is to address several key technical issues and challenges associated with the characterization, design, and development of ILs as new monopropellants. Among these, for example, are a fundamental understanding of the (in)stability of ILs, the intrinsic nature of the short- and long-range structure and interactions between the component ions, and identification of the key steps in the initial stages of decomposition and combustion. A hierarchy of computational approaches is employed, including atomistic, high-level quantum chemical methods applied to individual ions and ion clusters, condensed phase atomistic molecular dynamics simulations utilizing polarizable force fields, and mesoscale-level simulations of bulk ionic liquids based upon multiscale coarse graining techniques.

1. Introduction

The design of new high energy density materials, which are more efficient, reliable, and environmentally benign than existing rocket propellants, is a high DoD priority. The focus of this effort has been on the development of new propellants and energetic additives, including highly strained hydrocarbons, polynitrogen compounds, and advanced monopropellants. Some of the issues that must be addressed in theoretical efforts to design new energetic materials include an assessment of their energy content, their thermodynamic and kinetic stability, and the design of new synthetic routes to proposed new compounds that have not yet been synthesized.

A specific area of interest to the DoD is the discovery of a suitable replacement for hydrazine, a widely used monopropellant for low-thrust propulsion applications such as orbital maneuvering and satellite stationkeeping. The desire to replace hydrazine is motivated by several factors. Perhaps the most severe limitation of hydrazine is its carcinogenic nature and extreme respiratory and dermatological toxicity, with correspondingly large costs

associated with controlling these environmental and biological hazards. Furthermore, the performance of hydrazine as a monopropellant is rather modest due to its relatively low density and specific impulse compared to a prototypical ionic monopropellant salt such as 4-amino-1,2,4-triazolium dinitramide. The replacement of hydrazine with more energetic, less hazardous energetic monopropellants is clearly needed.

A specific type of energetic material of current interest is derived from a broad class of compounds known generically as ionic liquids (ILs), which are chemical salts with unusually low melting points; e.g., below 100° C. The general interest in ILs has focused mainly on their use as environmentally benign ("green") solvents for a wide range of chemical reactions. Some of the properties of ILs which make them attractive as solvents include their low vapor pressure, large liquid ranges, and thermal stability. The interest in ILs as new monopropellants stems from several factors. For example, the properties of ILs, including their energy content, can be "tuned" through a judicious choice of component ions and their substituents. Furthermore, the virtually nonexistent vapor pressure of ILs greatly reduces the environmental and biological hazards due to respiratory and dermatological toxicity. Finally, the densities of ILs generally are significantly greater than those of conventional liquid monopropellants such as hydrazine.

Although there have been extensive experimental studies of chemical reactions in ILs, little has been done in the area of characterization of the fundamental chemical and physical properties of ILs. In particular, one of the most pressing needs in the broader area of IL development, and particularly in the design of energetic ILs, is the application of robust theoretical methods for the reliable prediction of IL heats of formation, synthesis routes, phase transitions, ion conformations, thermal stabilities, densities, and viscosities. The focus of this study is on the characterization, design, and synthesis of the next generation of monopropellants for rocket propulsion applications.

2. Computational Methods

An integrated approach utilizing multiple computational methods is used to predict and characterize the intrinsic and bulk properties of energetic ionic liquids. At the molecular level, highly accurate electronic structure methods are used to predict the fundamental properties of the ionic liquid components, including molecular structures, charge delocalization, heats of formation, and proton transfer reaction pathways and barriers. Geometries, electronic structures, and properties (including heats of formation) of the component ions are predicted using second-order perturbation theory (MP2, also known as MBPT(2)[1]), density functional theory (DFT)[2], coupled cluster theory (CCSD(T)[3]) and the "Gaussian-N" (GN)[4] methods. The Nuclear-Electronic Orbital (NEO)[5] approach is used for capturing the quantum dynamical effects of hydrogen bonding and proton transfer. In addition, the complex spectrum of ionic liquid physical properties requires utilization of polarizable force fields in condensed phase simulations in order to obtain reliable predictions of many key bulk properties.

3. Results and Discussion

Cation-cation π-π Stacking: A theoeretical study[6] of the gas-phase geometries and interactions in small clusters of ions suggests the presence of π-π stacking structures between the cations in dimers of 1,2,4-triazolium dinitramide (two cations and two anions) as well as 1,2,4-triazolium chloride. These types of structures can be formed in dielectric solvents due to screening of the charge-charge repulsion forces,[7] but such species in small structures have not been previously reported.

Of the numerous structures found for the two pairs of 1,2,4-triazolium and dinitramide ions, or the pairs of corresponding neutral 1,2,4-triazole and dinitramine molecules, the most stable MP2/aug-cc-pvdz[8] optimized geometries are shown in Figure 1. In the ionic structure, each 1,2,4-triazolium forms two hydrogen bonds, via the hydrogens on the N atoms, to the O atoms of the dinitramide ions. Interestingly, this structure exhibits parallel stacking of the two cationic 1,2,4-triazolium rings. The interplane distance is ~3.2 Å, with a parallel displacement of ~1.4 Å. The corresponding neutral tetramer shows a similar parallel stacking arrangement of the triazole rings.

Furthermore, it is of interest to determine the cluster size at which the ion pair structures become more stable than the corresponding neutral pair structures. A previous study predicted that ion pair dimers are typically higher in energy than neutral pair dimers.[9] Including zero point vibrational energy (ZPVE) corrections, the ionic tetramer in Figure 1 is 1.2 kilocalorie / mole (kcal/mol) lower than that of the neutral one. The MP2 method tends to predict higher energies for ionic species vs. neutral species,[9] so more accurate CCSD(T)/aug-cc-pVDZ energy calculations of these two tetramer structures were desired. However, since the computational cost of CCSD(T)/aug-cc-pVDZ is prohibitive, these energies were approximated from the MP2/aug-cc-pVDZ energies by estimating the electron correlation energy differences using three independent methods: (1) the differences between the MP2/cc-pVDZ[8] and CCSD(T)/cc-pVDZ energies of the tetramers, (2) the differences between the MP2/aug-cc-pVDZ and CCSD(T)/aug-cc-pVDZ energies

of the twelve pairs of dimers in these two tetramers, and (3) the differences between the MP2/aug-cc-pVDZ and CCSD(T)/aug-cc-pVDZ energies of the eight monomers in these two tetramers. Using these three methods, and including ZPVE corrections, the estimated CCSD(T)/aug-cc-pVDZ energy of the ionic tetramer is lower than that of the neutral tetramer by 5.7, 7.3, and 7.7 kcal/mol, respectively.

The driving force for the formation of the unusual cation-cation π-π stacking structure is also very interesting. Geometry optimization of the ionic structure using Hartree-Fock, which does not contain electron correlation, results in an "open-book" structure in which the two 1,2,4-triazolium planes form a dihedral angle of ~120° (no π-π stacking). Clearly, electron correlation energy (a major part of the aromatic π-π attraction) in the MP2 method is the driving force for the formation of the cation-cation π-π stacking structure from the open-book non-stacking structure.

Figure 1. MP2/aug-cc-pVDZ optimized structures of two pairs of 1,2,4-triazolium (1,2,4-triazole) and dinitramide (dinitramine) molecules. H is white, C is gray, O is red, N is blue.

Top view   **Front view**
Ionic

Top view   **Front view**
Neutral
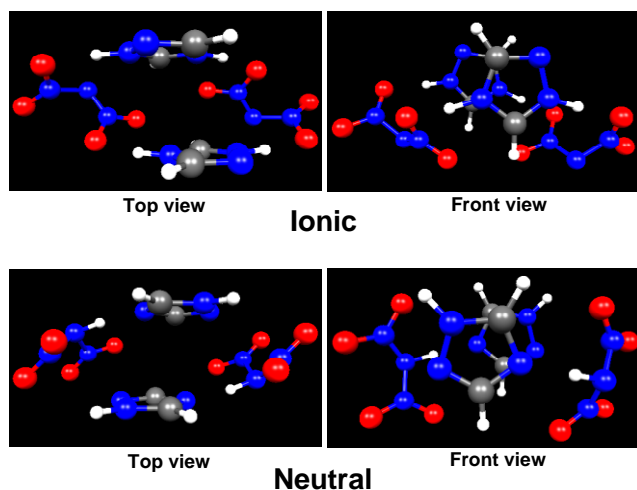
[Emim⁺][Im⁻] Ion Clusters: Ionic liquids such as 1-ethyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl) imide ([Emim⁺][Im⁻]) show great promise as advanced working fluids in electric propulsion applications. In order to assess and tune the performance of these types of working fluids, it is necessary to characterize the exhaust plume, which contains a distribution of clusters such as [Emim⁺]$_m$[Im⁻]$_{m\pm1}$; i.e., containing either an excess cation or anion. The gas-phase structures, harmonic vibrational frequencies, and binding energies of a series of ion clusters [Emim⁺]$_m$[Im⁻]$_{m\pm1}$ (m=1-3) were computed at the MP2/6-311++G(d,p)[10] level and compared to earlier

density functional theory (B3LYP/6-311++G(d,p)) calculations.[11] The MP2 predicted structures generally favor interactions between the anion and the π electron density of the cation ring, whereas the DFT geometries tend to favor interionic hydrogen bonding between the hydrogen atoms on the cation and the nitrogen or oxygen atoms of the anion. An example of this difference in predicted structures is illustrated in Figure 2, which shows the MP2 and DFT geometries of [Emim⁺][Im⁻]$_2$. Panels (a) and (b) ((c) and (d)) show two different views of the same B3LYP (MP2) local minimum. Panels (a) and (b) show a predominance of hydrogen bonding interactions between the hydrogen atoms on the [Emim⁺] cation and the oxygen atoms on the [Im⁻] anions. In contrast, the MP2 optimized geometry of [Emim⁺][Im⁻]$_2$ shown in panels (c) and (d) suggests the presence of interactions between the anions and the π electron density of the cation ring.

Figure 2. Calculated geometries of [Emim⁺][Im⁻]$_2$, B3LYP/6-311++G(d,p) (panels (a) and (b)) and MP2/6-311++G(d,p) (panels (c) and (d)). H, C, N, O, F, and S atoms are shown in white, black, blue, red, green, and yellow, respectively.

**B3LYP/6-311++G(d,p)**   **MP2/6-311++G(d,p)**
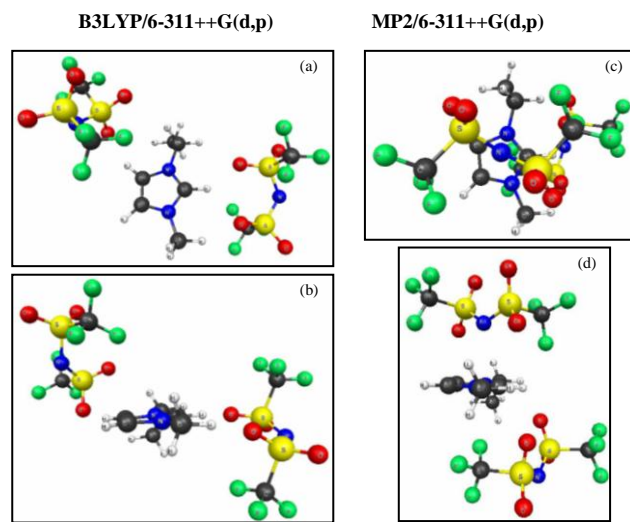
Molecular Dynamics Simulations of the Energetic Ionic Liquid 1-hydroxyethyl-4-amino-1, 2, 4-triazolium Nitrate (HEATN): Molecular dynamics (MD) simulations have been performed to investigate the structure and dynamics of an energetic ionic liquid, 1-hydroxyethyl-4-amino-1,2,4-triazolium nitrate (HEATN).[12] The generalized Amber force field (GAFF) was used, and an electronically polarizable model was further developed in the spirit of our previous work.[13] In the process of simulated annealing from a liquid state at 475 K down to a glassy state at 175 K, the MD simulations identify a glass-transition temperature region

at around 250-275 K, in agreement with experiment.[14] A complex hydrogen bond network was revealed with the calculation of partial radial distribution functions. When compared to the similarly sized 1-ethyl-3-methyl-1,3-imidazolium nitrate ionic liquid, $EMIM^+/NO_3^-$, a hydrogen bond network directly resulting in the poorer packing efficiency of ions is observed, which is responsible for the lower melting/glass-transition point. The structural properties of the liquid/vacuum interface shows that there is vanishing layering at the interface, in accordance with the poor ion packing. The effects of electronic polarization on the self-diffusion, viscosity, and surface tension of HEATN are found to be significant, in agreement with an earlier study on $EMIM^+/NO_3^-$.[15]

Based on a charge-removed force-matching procedure, a five-site coarse graining (CG) model has been constructed for HEATN. This model produces structural properties which are in good agreement with atomistic simulations (see Figure 3). The coarse graining results are also consistent with the strong screening effect in bulk HEATN. A striking feature of this CG model is spatial transferability. The force field developed by a system of 216 ion pairs has been successfully used in larger systems (343 and 512 pairs) to provide good structure properties as shown in Figure 3.[16] Another important point is the sharp peak of cation-anion correlation resulting from the CG simulation: the double peaks from the atomic simulation disappear because the coarse-graining procedure misses the oriented information involved in the highly delocalized $-NH_2 \cdots ONO_2^-$ and $-OH \cdots ONO_2^-$ hydrogen bonding interactions.[12,16]

Figure 3. Radial distribution functions g(r) of HEATN from molecular dynamics simulations utilizing atomistic and coarse-graining force field models.
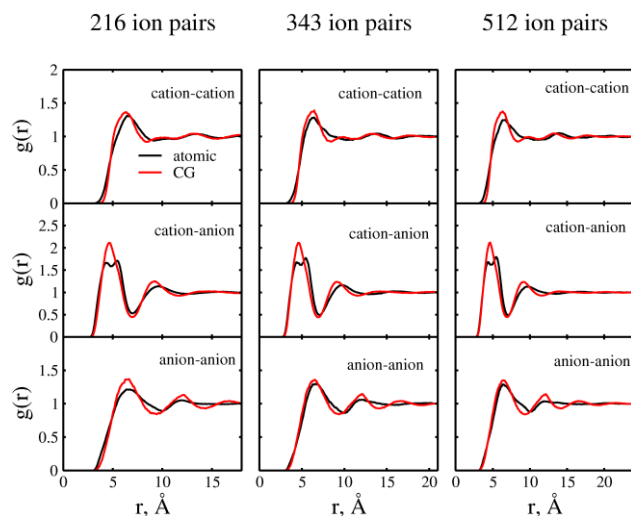
4. Summary and Conclusions

The geometries of the dimers of 1,2,4-triazolium dinitramide and 1,2,4-triazolium chloride have been computed at the MP2/aug-cc-pvdz level of theory. These calculations suggest that cation-cation π-π stacking structures can exist in very small ionic clusters. Electron correlation energy in the MP2 method is the driving force for the formation of the cation-cation π-π stacking structure from the open-book non-stacking structure. The structure motifs and interaction patterns provide new understanding of ionic materials with aromatic rings.

The structures, harmonic vibrational frequencies, binding energies, and internal thermal energy distributions of gas-phase ion clusters of the 1-ethyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide ionic liquid have been predicted using second order perturbation theory (MP2/6-311++G(d,p)) and compared to prior density functional theory (B3LYP/6-311++G(d,p)) results. The MP2 predicted structures generally favor interactions between the anion and the π electron density of the cation ring, whereas the DFT geometries tend to favor interionic hydrogen bonding interactions.

Classical molecular dynamics simulations of HEATN predict the presence of a glass transition at a temperature of about 275 K, in agreement with experiment. Utilization of a polarizable versus a nonpolarizable force field resulted in significant differences in predicted transport properties such as self-diffusion coefficients and shear viscosity. Simulations based upon a five-site CG model predict structural properties in good agreement with atomistic results and also show spatial transferability of the CG model to larger systems.

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